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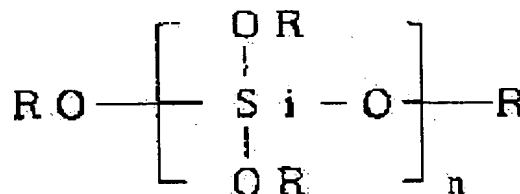
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(54) STAINPROOF PAINTING AGENT COMPOSITION FOR SURFACE OF STRUCTURE AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a stainproof painting agent composition capable of exhibiting hydrophilicity and stainproof property directly after the painting on the surface of a structure without needing an acid treatment or the like, excellent in storage stability, drying property and handleability, and capable of forming paint film excellent in adhesivity and transparency, and having good appearance, and to provide a method for manufacturing the composition.

SOLUTION: An organo silicate of the general formula 1 (wherein, R is a 1-10C hydrocarbon group; and n is an integer of ≥ 1) is hydrolyzed in the presence of an acid catalyst so that the amount of hydrolyzing water is 60-600 pts.wt. based on 100 pts.wt. of the Si in the organo silicate in terms of SiO₂, and a water-containing diluent is added to the obtained hydrolyzate so that the water content after the adjustment is 600-4,000 pts.wt. based on 100 pts.wt. of the Si in the organo silicate in terms of SiO₂.



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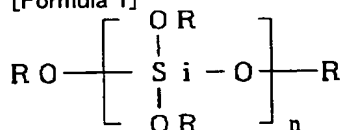
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CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1)

[Formula 1]



(However, among the formula, R shows the hydrocarbon group of carbon numbers 1-10, and even if it is mutually the same, it may differ.) moreover, n shows one or more integers. The ORGANO silicate expressed is hydrolyzed with the water of the hydrolysis moisture content of the 60 - 600 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of a hydrolysis catalyst. Moisture adjustment is carried out so that a water content diluent may be added to the obtained hydrolysis reactant and the moisture content after adjustment may serve as the range of the 600 - 4000 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate. The paint agent constituent for pollution controls on the front face of the structure characterized by containing the obtained moisture adjustment constituent as a principal component.

[Claim 2] The paint agent constituent for pollution controls on the front face of the structure according to claim 1 whose hydrolysis moisture content introduced into the hydrolysis system of reaction is the 120 - 400 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate.

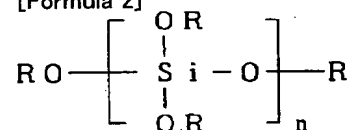
[Claim 3] The paint agent constituent for pollution controls on the front face of the structure according to claim 1 or 2 whose moisture content after adjustment is the 1000 - 3500 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate.

[Claim 4] The paint agent constituent for pollution controls on the front face of the structure according to claim 1 to 3 which has the coat as which the structure front face was chosen from a fluororesin coating, polyurethane resin enamels and varnishes, acrylic plastic paint, a polyester resin coating, and aqueous plastic paint.

[Claim 5] The paint agent constituent for pollution controls on the front face of the structure according to claim 1 to 4 which shifts and is formed with that construction material which the base material of the structure should choose from a metal, glass, a low, the ceramics, concrete, timber, and plastics.

[Claim 6] The following general formula (1)

[Formula 2]



(However, among the formula, R shows the hydrocarbon group of carbon numbers 1-10, and even if it is mutually the same, it may differ.) moreover, n shows one or more integers. The ORGANO silicate expressed is hydrolyzed with the water of the hydrolysis moisture content of the 60 - 600 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of a hydrolysis catalyst. Subsequently, moisture adjustment is carried out so that a water content diluent may be added to the obtained hydrolysis reactant and the moisture content after adjustment may serve as the range of the 600 - 4000 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate. The manufacture approach of the paint agent constituent for pollution controls on the front face of the structure characterized by making the obtained moisture adjustment constituent contain as a principal component.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Although this invention relates to the paint agent constituent for pollution controls used in order to prevent that the front face of the structure is polluted, especially is not limited, it is applied to an outdoor structure front face, and relates that this structure front face is polluted by causes of contamination, such as soot and exhaust gas, to the paint agent constituent for pollution controls and its manufacture approach on the front face of the structure prevented as much as possible.

[0002]

[Description of the Prior Art] When contamination causative agents, such as soot and exhaust gas, tend to adhere and these contamination causative agent adheres to the painted surface of a building, it flows out at the time of a rainfall, and on a painted surface, it becomes dirt of the shape of a black muscle, and appears, and there is a problem of spoiling the fine sight of the painted surface of a building remarkably in the front face of the structures, such as a building, especially the painted surface of the building always put outdoors to causes of contamination, such as soot and exhaust gas.

[0003] Then, in the former, the fluorine system coating agent by which alkyl silicate or its condensate was added by the hydrophobic fluororesin coating as an approach for preventing contamination of the painted surface of such a building as much as possible is proposed (each official report of JP,8-120,211,A, JP,8-120,212,A, and JP,8-176,304,A).

[0004] However, although, as for these fluorine system coating agents, alkyl silicate or its condensate is added and a certain amount of contamination improves, it originates in a hydrophobic, powerful fluororesin coating, a long period of time is taken for a front face to present a hydrophilic property, the antifouling property-proof in the first stage after paint film formation is low, soiling due to rain trace tends to adhere in the early stages of a pole, and contamination of the painted surface of a building cannot be prevented thoroughly. For this reason, it must be said that it is what betrays expectation of an original pollution control also temporarily.

[0005] Moreover, recently, in aiming at low contamination and un-polluting, it has turned out that it is more effective to be concordance-easy in water (hydrophilic property), and to make it it rather (February 10, 1995 issuance "monthly building material news" the 18 - 19th page). It originates in dirt being permuted by storm sewage, and electric resistance flowing and falling, when ** storm sewage with which it cannot enter easily into a paint film since concordance with a paint film is bad even if ** dust and dirt to which neither dust nor dirt can adhere easily adhere, since ** hydrophilic-property paint film cannot be charged easily low hits.

[0006] And as an approach of obtaining such a hydrophilic paint film, paint the primer, it comes to blend ORGANO silicate and/or its condensate with an organic silicon hardening mold solvent system coating on it, and the method of painting, and stiffening continuously the top coat whose contact angle over the water of the hardening paint film front face after acid treatment is 70 or less degrees is proposed (JP,7-136,584,A and the patent No. 2,869,443 printing official report). However, by this approach, in order to give a hydrophilic property to top coat, acid treatment of the front face of the hardening paint film after spreading must be carried out, and there is a problem that down stream processing increases so much and costs also increase.

[0007] Moreover, applying the hydrolysis reactant obtained on the structure front face by hydrolyzing ORGANO silicate with the water of 3 - 70 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of an acid catalyst as an approach of preventing the dirt resulting from the dust produced on a finishing paint film front face, an oily component, etc. is also proposed (JP,7-136,583,A). However, in this approach, since there is little water used for hydrolysis, even if an alkoxy group remains in the obtained hydrolyzate, it hydrolyzes with the moisture in air with the passage of time after paint and a hydrophilic property may be acquired, a hydrophilic property may not be acquired immediately after paint and pollution-control effectiveness sufficient as a result may not be acquired.

[0008]

[Problem(s) to be Solved by the Invention] Then, this invention persons give a hydrophilic property to the front face of a hardening paint film, without needing such acid treatment. The result of having examined wholeheartedly the paint agent constituent for pollution controls on the front face of the structure which can make the resistance to contamination excellent in the structure front face demonstrate, ORGANO silicate is hydrolyzed with the water of extent which is not gelled under existence of a hydrolysis catalyst. subsequently, the moisture adjustment constituent which diluted the obtained hydrolysis reactant with the water content diluent, and was adjusted to the predetermined moisture content not only demonstrates the resistance to contamination which demonstrated the hydrophilic property and was excellent from immediately after paint, but A header and this invention were completed for it having storage stability and drying, excelling in handling nature, it excelling also in the adhesion and transparency over a hardening paint film moreover, and the good paint film of an appearance being formed.

[0009] Therefore, while the object of this invention can make the resistance to contamination which could give the hydrophilic property to the structure front face from immediately after paint, and was excellent in the structure front face with this demonstrate, without needing special processing of acid treatment etc. It is in offering the paint agent constituent for pollution controls on the front face of the structure which has drying [excellent in coincidence / storage stability or drying], is excellent in handling nature, is moreover excellent also in adhesion or transparency, and can form the good paint film of an appearance.

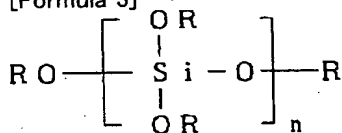
[0010] Moreover, other objects of this invention are to offer the manufacture approach of the paint agent constituent

for pollution controls on the front face of the structure which can give a hydrophilic property to a structure front face from immediately after paint, without needing special processing of acid treatment etc., is excellent in resistance to contamination, storage stability, handling nature, adhesion, and transparency, and can form the good paint film of an appearance.

[0011]

[Means for Solving the Problem] That is, this invention is the following general formula (1).

[Formula 3]



(However, among the formula, R shows the hydrocarbon group of carbon numbers 1-10, and even if it is mutually the same, it may differ.) moreover, n shows one or more integers. The ORGANO silicate expressed is hydrolyzed with the water of the hydrolysis moisture content of the 60 - 600 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of a hydrolysis catalyst. Moisture adjustment is carried out so that a water content diluent may be added to the obtained hydrolysis reactant and the moisture content after adjustment may serve as the range of the 600 - 4000 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate. It is a paint agent constituent for pollution controls on the front face of the structure which contains the obtained moisture adjustment constituent as a principal component. Moreover, this invention is the manufacture approach of the paint agent constituent for pollution controls on such a front face of the structure.

[0012] In this invention, as ORGANO silicate expressed with a general formula (1) An alkyl group, an allyl group, an aryl group, etc. are illustrated as the hydrocarbon group R. More specifically As an alkyl group, for example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, tert-butyl, n-pentyl radical, A vinyl group etc. can be mentioned [as an iso-pentyl radical, a neo-pentyl radical n-hexyl group, an iso-hexyl group, etc. and an allyl group], respectively as a phenyl group, a toluyl radical, a xylyl group, a naphthyl group, etc. and an aryl group. It is the alkyl group of carbon numbers 1-4 especially preferably from a viewpoint of being easy to hydrolyze in these.

[0013] Moreover, about the above-mentioned ORGANO silicate, it may be the monomer of n= 1, it may be the condensation product of n=2-10, or you may be such mixture further.

[0014] The paint agent constituent for pollution controls of this invention hydrolyzes the above-mentioned ORGANO silicate with the water of the hydrolysis moisture content of the 60 - 600 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of a hydrolysis catalyst. Carry out moisture adjustment and let the obtained moisture adjustment constituent be a principal component so that you may add a water content diluent to the obtained hydrolysis reactant and the moisture content after adjustment may serve as the range of the 600 - 4000 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate.

[0015] the hydrolysis moisture content used for hydrolyzing this ORGANO silicate here — — it is the amount which is extent which is more than the amount of theory in which 60 - 600 weight section" can hydrolyze this ORGANO silicate thoroughly, and the obtained hydrolysis reactant does not gel to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate, and it is preferably good that they are below the 400 weight sections more than the 120 weight sections. Since it will become easy to gel a hydrolysis reactant if hydrolysis will not fully progress if there are few these hydrolysis moisture contents than 60 weight sections, but the problem that a desired hydrophilic property is not acquired arises and it increases more than the 600 weight sections reversely, it is not desirable. In addition, in case this hydrolysis moisture content hydrolyzes ORGANO silicate, it means the amount of the total moisture which exists in that system of reaction, and it means all the moisture contents not only containing the water added by the hydrolysis system of reaction as a reaction agent but the water introduced into this hydrolysis system of reaction with a hydrolysis catalyst or a reaction solvent.

[0016] Moreover, as a hydrolysis catalyst used for the hydrolysis reaction of ORGANO silicate, although there is especially no limit, they are acid catalysts, such as organic acids, such as mineral acids, such as a nitric acid, a sulfuric acid, a hydrochloric acid, and phosphoric acid, and formic acid, an acetic acid, preferably. In the case of an acid catalyst, if it is usually 0.05 - 2 % of the weight preferably 0.01 to 5% of the weight, the problem that a hydrolysis rate becomes slow will arise in the system of reaction if fewer than 0.01 % of the weight, and the amount of this hydrolysis catalyst used increases more than 5 % of the weight reversely, a hydrolysis reactant will become easy to gel it, and also the problem that control of a reaction becomes difficult produces it.

[0017] Furthermore, if it is good to use the reaction solvent in which the ORGANO silicate and water of the system of reaction are made to dissolve mutually preferably on the occasion of the hydrolysis reaction of ORGANO silicate and it makes these both of each other dissolve as this reaction solvent, there will be especially no limit, but when the handling nature at the time of paint etc. is taken into consideration, alcohols are preferably good and, specifically, ethyl alcohol, iso-propyl alcohol, butyl alcohol, etc. are desirable. To the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate, it is the 200 - 2000 weight section preferably, and the 100 - 3000 weight section and the problem of being easy to gel if fewer than the 100 weight sections usually arise, and if it increases more than the 3000 weight sections reversely, a reaction will become inadequate, and also the problem that a reaction rate becomes slow produces the amount of this reaction solvent used.

[0018] the hydrolysis reactant obtained by this hydrolysis reaction — a water content diluent — adding — the moisture content after that adjustment — the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate — receiving — the 600 - 4000 weight section — let preferably the 1000 - 3500 weight section and the moisture adjustment constituent which moisture adjustment was carried out and were obtained be the principal components of the paint agent constituent for pollution controls on the front face of the structure of this invention so that you may become the range of the 1500 - 3000 weight section more preferably. Here, when there are few moisture contents after this adjustment than the 600 weight sections, an alkoxy group remains eventually, there is a problem that a desired hydrophilic property is not acquired, and if it increases more than the 4000 weight sections reversely, the problem that storage stability falls and a product life becomes short will arise.

[0019] If the water content diluent used for this moisture adjustment melts a hydrolysis reactant and each other's water, there will be especially no limit, but when it is good to use the thing of an organic solvent-drainage system and it

takes the dryness of the paint film after paint into consideration as this organic solvent, alcohols especially ethyl alcohol, iso-propyl alcohol, butyl alcohol, etc. are desirable like the case of a reaction solvent. Moreover, to the paint agent constituent of this invention, other solvents, such as alcohols, such as ethyl alcohol, iso-propyl alcohol, and butyl alcohol, and a solvent with high viscosity, a high solvent of the boiling point, may be added in order to adjust the rate of drying of the object for viscosity control, or a paint film as occasion demands.

[0020] As a structure front face where the paint agent constituent for pollution controls of this invention is applied For example, non-equipment-and-materials front faces, such as concrete, fiber-reinforced concrete, a slate, and glass, Acrylic resin, a fluororesin, polyurethane resin, polyester resin, The film fabricated by resin, such as polycarbonate resin, vinyl chloride resin, and polyethylene resin, Organic material front faces, such as resin mold goods, such as a sheet, and rubber goods, and aluminum, Organic inorganic composite front faces, such as organic inorganic composites, such as fiber consolidation resin, are begun further. metal material front faces, such as iron, stainless steel, a zinc steel plate, and a steel plate, — The painted surface which prepared beforehand the coat chosen from a fluororesin coating, polyurethane resin enamels and varnishes, acrylic plastic paint, a polyester resin coating, and aqueous plastic paint in the front face of these inorganic material, organic material, and organic inorganic composite can be mentioned. In these structure front faces, you may paint, after painting the paint agent constituent of this invention directly and carrying out surface treatment, such as a primer, or after carrying out an under coat.

[0021] The paint agent constituent for pollution controls of this invention For example, a structural skin panel, tentorium, A tarpaulin, a windshield sheet, a structural sheet, roofing, a skylight, a concrete wall, Structural members, such as a flush tank, a tank, a shutter, and a sash, a building outer wall, By painting in the part which the dirt of various outdoor articles, such as route members, such as a guard rail, a footbridge, an outer casing, a translucent plate, a noise buffer wall, an indicator, a high-speed path road-side wall, a tunnel wall surface, a railroad viaduct, and a bridge, tends to generate, it can continue extremely at a long period of time, and generating of dirt can be prevented.

[0022] The paint agent constituent for pollution controls of this invention can be easily painted by the paint by the usual method of application, for example, brush coating, roller coating, spray coating, the flow coater, the gravure coating machine, and the spin coat etc. Moreover, although ordinary temperature is sufficient as the desiccation approach and it may be heated, a dry paint film is obtained for the heated direction for a short period of time.

[0023] In the paint agent constituent for pollution controls of this invention, in spite of containing a lot of water Although the reason which exists in stability is not necessarily clear, without a hydrolysis reactant gelling If the polycondensation of the ORGANO silicate is beforehand hydrolyzed and carried out with the reaction water which is extent which hydrolyzes ORGANO silicate thoroughly and a hydrolysis reactant does not gel Although a polymerization reaction progresses and the hydrolysis reactant of this colloidal state forms a polymerization object in the beginning when the hydrolysis product generated by the reaction in the hydrolysis reactant will be in a spherical colloidal state, it distributes in a water content solvent and a lot of water is added here It is thought that this polymerization object exists in stability comparatively although static reaction with the water which exists so much hydrolyzes and a lot of water as a result exists.

[0024] [Example] Hereafter, based on an example and the example of a comparison, this invention is explained concretely. In 1500ml three necked flask of examples, taught 40g (the trade name by Tama chemical-industry incorporated company: ES-40, average degree of polymerization 4-5) of oligomer objects of ethyl silicate, and ethanol 88g, mixed to homogeneity, added 21.6g of pure water, and 28g of 6wt%-nitric acids as a catalyst here, and it was made to react to the bottom of heating reflux for 4 hours, it cooled, and the hydrolysis reactant (the 1st reactant) was obtained.

[0025] Next, the water content diluent obtained in the 1st obtained reactant by fully carrying out churning mixing of isopropyl alcohol 190g and the 430g of the pure water was added, churning mixing was carried out further, and it considered as the paint agent constituent of an example 1.

[0026] It replaced with ES-40 in the example 2 1st reaction mixture, and the paint agent constituent of an example 2 was prepared like the example 1 except having added 31.4g (the trade name by Tama chemical-industry incorporated company: MS-51, average degree of polymerization 3-4) of oligomer objects of methyl silicate.

[0027] The paint agent constituent of an example 3 was prepared like the example 1 except having set the pure water in an example 3 water content diluent to 272g.

[0028] The paint agent constituent of an example 4 was prepared like the example 1 except having set the pure water in an example 4 water content diluent to 112g.

[0029] The paint agent constituent of an example 5 was prepared like the example 1 except having set the pure water in an example 5 water content diluent to 48g.

[0030] Although prepared 40g, ethanol 88g, isopropyl alcohol 190g, and 650g of pure water, ES-40 were mixed to homogeneity, 28g of 6wt%-nitric acids was subsequently added in 11500ml three necked flask of examples of a comparison and it was made to react to the bottom of heating reflux for 4 hours, reaction mixture was gelled on the way.

[0031] Unlike the water content diluent used in the example of comparison 2 example 1, the paint agent constituent of the example 2 of a comparison was prepared like the example 1 except having used only isopropyl alcohol 19g as a diluent.

[0032] It verified about each paint agent constituent of the [verification of test-result/example] above-mentioned examples 1-5, and the example 2 of a comparison. after putting storage stability into a container, sealing a paint agent constituent and holding for three months at the temperature of 40 degrees C — a room temperature — returning — the condition in a container — observing — O: — O: in which change is not accepted at all — a little — the white taste — **** and **: — it becomes muddy white and evaluated in four steps of ** of which x: gelation was done. Moreover, the paint agent constituent was painted on the glass plate, and drying, transparency, and an appearance were observed visually. Membranes are not dried and formed 1 hour after x:, but it evaluates in two steps of **. And it dried and formed membranes thoroughly 1 hour after O: about drying, about transparency O The three-stage of ** which wears the white taste 1 hour after x: which becomes transparency 1 hour after : and which wears the white taste a little 1 hour after **: estimated, and it evaluated in two steps of ** powdered without having formed membranes thoroughly 1 hour after O: about the paint film appearance, and drying and forming membranes 1 hour after x:. The above result is shown in a table 1.

[0033]

[A table 1]

| | 調整後水分量(*1) | 貯蔵安定性 | 乾燥性 | 透明性 | 塗膜外観 |
|-------|------------|--------|-----|-----|------|
| 実施例 1 | 3000 | ◎ | ◎ | ◎ | ◎ |
| 〃 2 | 〃 | ◎ | ◎ | ◎ | ◎ |
| 〃 3 | 2000 | ◎ | ◎ | ◎ | ◎ |
| 〃 4 | 1000 | ○ | ◎ | ◎ | ◎ |
| 〃 5 | 600 | △ | ◎ | △ | ◎ |
| 比較例 1 | 4000 | 合成時ゲル化 | | | |
| 〃 2 | 300 | × | × | × | × |

(注) *1) 原料オルガノシリケート中 Si 原子の SiO₂ 換算 100 重量部に対する調整後水分量 (重量部)

[0034] Furthermore, as shown in a table 2, on the substrate with which a solvent fluoro-resin coating, solvent polyurethane resin enamels and varnishes, the printing fluoro-resin coating, and the printing polyester resin coating were applied, respectively, the aluminum plate, the vinyl chloride plate, or the polycarbonate plate, the paint agent constituent of each above-mentioned examples 1-6 and the example 2 of a comparison was painted at a rate of 0.03kg/m², and the test piece of examples 1-5 and the example 2 of a comparison was prepared.

[0035] About the test piece of each acquired examples 1-5 and the example 2 of a comparison, the painted surface is exposed to the outdoors, and it is ***** about a direct weathering test. Assessment of the dirt by this direct weathering test made **L* the difference of the lightness exposure [six months after] before and after exposure. The color color difference meter (CR[by Minolta Co., Ltd.]- 300) performed measurement of this lightness difference, and more than O:-2, O:-2-5, **: -5-8, and the criteria not more than x:-8 estimated. In addition, lightness difference **L* shows that dirt has few bigger numeric values.

[0036] Moreover, the initial-contact angle in front of an outdoor exposure was measured as a degree of a hydrophilic property. Measurement of this contact angle trickled 0.02 cc deionized water on the above-mentioned painted surface, and measured the contact angle of waterdrop at 20 degrees C using the contact angle measuring device (the trade name by consonance chemistry incorporated company: CONTACT-ANGLEMETER CA-A mold). The result of these three-point measurement averages is shown in a table 2.

[0037]

[A table 2]

| | | 実 施 例 | | | | | 比較例 |
|--------------|------|-------|----|----|----|----|-----|
| | | 1 | 2 | 3 | 4 | 5 | 2 |
| 溶剤フッ素樹脂塗料 | 接触角 | 28 | 36 | 36 | 58 | 81 | 92 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ○ | △ | × |
| 溶剤ポリウレタン樹脂塗料 | 接触角 | 37 | 33 | 65 | 65 | 78 | 88 |
| | 屋外暴露 | ◎ | ◎ | ○ | ○ | △ | × |
| 焼付フッ素樹脂塗料 | 接触角 | 40 | 31 | 48 | 50 | 75 | 93 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ○ | △ | × |
| 焼付ポリウレタン樹脂塗料 | 接触角 | 15 | 23 | 45 | 52 | 78 | 93 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ○ | △ | × |
| アルミ板 | 接触角 | 35 | 35 | 55 | 53 | 75 | 89 |
| | 屋外暴露 | ◎ | ◎ | ○ | ○ | △ | × |
| 硬質塩ビ板 | 接触角 | 33 | 35 | 53 | 55 | 75 | 95 |
| | 屋外暴露 | ◎ | ◎ | ○ | ○ | △ | × |
| ポリカーボネート板 | 接触角 | 10 | 10 | 34 | 38 | 70 | 90 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ◎ | △ | △ |

[0038] Since the paint film from which the paint agent constituent of each examples 1-5 was obtained using this is a hydrophilic property so that clearly from the result of the above-mentioned table 1 and a table 2, dirt will be permuted by this storm sewage by hitting, storm sewage will flow and fall, resistance to contamination continues, and is demonstrated at a long period of time, and contamination on the front face of the structure can be prevented effectively.

[0039] The 40g of the same oligomer objects of ethyl silicate as having used in the example 1 into 32000ml three necked flask of examples of a comparison, Teach ethanol 88g and isopropyl alcohol 190g, and it mixes to homogeneity. Add 453g of pure water, and 28g of 6wt%-nitric acids as a catalyst here, and it was made to react to the bottom of heating reflux for 4 hours, and it cooled and the hydrolysis reactant (paint agent constituent) whose moisture content is the 3000 weight sections eventually was obtained to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate.

[0040] It replaced with the oligomer object of example of comparison 4 ethyl silicate, and the paint agent constituent of the example 4 of a comparison whose moisture content is the 3000 weight sections eventually was prepared like the example 3 of a comparison to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate except having used 31.4g of oligomer objects of the same methyl silicate with having used in the example 2.

[0041] The paint agent constituent of the example 5 of a comparison whose moisture content is the 2000 weight sections eventually was prepared like the example 3 of a comparison to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate except having set the amount of example of comparison 5 pure water used to 293g.

[0042] About each paint agent constituent of the [verification of test-result/example] above-mentioned examples 1-3, and the examples 3-5 of a comparison, the adhesion, the initial hydrophilic property (contact angle), and the appearance of the paint film before and behind a three-month outdoor exposure and a hydrophilic property (contact angle) were evaluated, and the appearance of the paint film before and behind a six-month outdoor exposure, assessment (lightness difference **L*) of dirt, and a hydrophilic property (contact angle) were verified further. A result is shown in a table 3.

[0043] Under the present circumstances, measurement of outdoor-exposure, contact angle, and lightness difference **L* and assessment of a paint film appearance On a substrate, apply a solvent fluororesin coating (the trade name by coating A; Atomix Co., Ltd.: atom SEFURONH), or solvent polyurethane resin enamels and varnishes (the trade name by coating B; Atomix Co., Ltd.: life tex #70) on condition that 30-micrometer coating [1 time], respectively, and a painted surface is formed. The paint agent constituent of each above-mentioned examples 1-3 and the examples 3-5 of a comparison was painted at a rate of 0.03 g/m² on this painted surface, and it carried out by preparing the test piece of each examples 1-3 and the examples 3-5 of a comparison.

[0044] About adhesion, in addition, about the test piece of each above-mentioned examples 1-3 and the examples 3-5 of a comparison According to JIS K5400 8.5.3, it measures by the X cut tape method. 10 : There is no peeling in 8:intersection when peeling is not accepted at all, and peeling is slightly accepted in X cut section. Peeling of 1.5mm or less is accepted in the direction of either from the intersection of the 6:X cut section. 4: The viewpoint with which exceed 1.5mm in the direction of either from the intersection of X cut section, and peeling of 3.0mm or less is accepted to be and peeling is accepted to be to the great portion of 2:X cut section of separating more greatly than the 0:X cut section estimated.

[0045] moreover, the test piece (the include angle between a vertical plane and an inclined plane: 135 degrees) which has a vertical plane in the lower part while a direct weathering test has a 45-degree inclined plane in the upper part, as shown in drawing 1 — preparing — a vertical plane — the appearance of a paint film — moreover, the dirt of a paint film was evaluated in the inclined plane, respectively. the appearance of the paint film after this outdoor exposure — visual observation — O: — O: in which a rain trace is not accepted at all — **: a thin rain trace is accepted to be to a part — it evaluated in four steps of ** where a rain trace is accepted all over [on which the rain trace which clarified to the part is accepted] x:.

[0046]

[A table 3]

| | | | 実施例 | | | 比較例 | | |
|------|----------------------------|--------|------|------|------|------|------|------|
| | | | 1 | 2 | 3 | 3 | 4 | 5 |
| 塗料 A | 密着性 | | 10 | 10 | 10 | 8 | 8 | 8 |
| | 接触角 | 初期 | 28 | 36 | 36 | 80 | 81 | 81 |
| | | 3ヶ月暴露後 | 25 | 30 | 32 | 76 | 78 | 79 |
| | | 6ヶ月暴露後 | 17 | 25 | 25 | 65 | 65 | 67 |
| | 塗膜の外観 (*1) | 3ヶ月暴露後 | ◎ | ◎ | ◎ | × | × | × |
| | | 6ヶ月暴露後 | ◎ | ◎ | ◎ | △ | △ | △ |
| | 6ヶ月暴露前後の汚れ評価 (明度差△L*) (*2) | | -0.4 | -0.8 | -0.9 | -5.7 | -5.8 | -6.7 |
| 塗料 B | 密着性 | | 10 | 10 | 10 | 0 | 4 | 6 |
| | 接触角 | 初期 | 37 | 33 | 65 | 79 | 79 | 81 |
| | | 3ヶ月暴露後 | 25 | 29 | 45 | 77 | 77 | 78 |
| | | 6ヶ月暴露後 | 18 | 24 | 35 | 65 | 65 | 68 |
| | 塗膜の外観 (*1) | 3ヶ月暴露後 | ◎ | ◎ | ○ | × | × | × |
| | | 6ヶ月暴露後 | ◎ | ◎ | ◎ | △ | △ | △ |
| | 6ヶ月暴露前後の汚れ評価 (明度差△L*) (*2) | | -0.3 | -0.3 | -1.2 | -6.0 | -6.0 | -6.5 |

[0047]

[Effect of the Invention] The paint agent constituent for pollution controls of this invention can give a hydrophilic property to a structure front face from immediately after paint, without needing special processing of acid treatment etc., it has drying [excellent in coincidence / storage stability or drying], and excels in handling nature, and moreover, is excellent also in adhesion or transparency and can form the good paint film of an appearance while making the resistance to contamination which was excellent in the structure front face with this demonstrate.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] Although this invention relates to the paint agent constituent for pollution controls used in order to prevent that the front face of the structure is polluted, especially is not limited, it is applied to an outdoor structure front face, and relates that this structure front face is polluted by causes of contamination, such as soot and exhaust gas, to the paint agent constituent for pollution controls and its manufacture approach on the front face of the structure prevented as much as possible.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] When contamination causative agents, such as soot and exhaust gas, tend to adhere and these contamination causative agent adheres to the painted surface of a building, it flows out at the time of a rainfall, and on a painted surface, it becomes dirt of the shape of a black muscle, and appears, and there is a problem of spoiling the fine sight of the painted surface of a building remarkably in the front face of the structures, such as a building, especially the painted surface of the building always put outdoors to causes of contamination, such as soot and exhaust gas.

[0003] Then, in the former, the fluorine system coating agent by which alkyl silicate or its condensate was added by the hydrophobic fluororesin coating as an approach for preventing contamination of the painted surface of such a building as much as possible is proposed (each official report of JP,8-120,211,A, JP,8-120,212,A, and JP,8-176,304,A).

[0004] However, although, as for these fluorine system coating agents, alkyl silicate or its condensate is added and a certain amount of contamination improves, it originates in a hydrophobic, powerful fluororesin coating, a long period of time is taken for a front face to present a hydrophilic property, the antifouling property-proof in the first stage after paint film formation is low, soiling due to rain trace tends to adhere in the early stages of a pole, and contamination of the painted surface of a building cannot be prevented thoroughly. For this reason, it must be said that it is what betrays expectation of an original pollution control also temporarily.

[0005] Moreover, recently, in aiming at low contamination and un-polluting, it has turned out that it is more effective to be concordance-easy in water (hydrophilic property), and to make it it rather (February 10, 1995 issuance "monthly building material news" the 18 - 19th page). It originates in dirt being permuted by storm sewage, and electric resistance flowing and falling, when ** storm sewage with which it cannot enter easily into a paint film since concordance with a paint film is bad even if ** dust and dirt to which neither dust nor dirt can adhere easily adhere, since ** hydrophilic-property paint film cannot be charged easily low hits.

[0006] And as an approach of obtaining such a hydrophilic paint film, paint the primer, it comes to blend ORGANO silicate and/or its condensate with an organic silicon hardening mold solvent system coating on it, and the method of painting, and stiffening continuously the top coat whose contact angle over the water of the hardening paint film front face after acid treatment is 70 or less degrees is proposed (JP,7-136,584,A and the patent No. 2,869,443 printing official report). However, by this approach, in order to give a hydrophilic property to top coat, acid treatment of the front face of the hardening paint film after spreading must be carried out, and there is a problem that down stream processing increases so much and costs also increase.

[0007] Moreover, applying the hydrolysis reactant obtained on the structure front face by hydrolyzing ORGANO silicate with the water of 3 - 70 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of an acid catalyst as an approach of preventing the dirt resulting from the dust produced on a finishing paint film front face, an oily component, etc. is also proposed (JP,7-136,583,A). However, in this approach, since there is little water used for hydrolysis, even if an alkoxy group remains in the obtained hydrolyzate, it hydrolyzes with the moisture in air with the passage of time after paint and a hydrophilic property may be acquired, a hydrophilic property may not be acquired immediately after paint and pollution-control effectiveness sufficient as a result may not be acquired.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The paint agent constituent for pollution controls of this invention can give a hydrophilic property to a structure front face from immediately after paint, without needing special processing of acid treatment etc., it has drying [excellent in coincidence / storage stability or drying], and excels in handling nature, and moreover, is excellent also in adhesion or transparency and can form the good paint film of an appearance while making the resistance to contamination which was excellent in the structure front face with this demonstrate.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Then, this invention persons give a hydrophilic property to the front face of a hardening paint film, without needing such acid treatment. The result of having examined wholeheartedly the paint agent constituent for pollution controls on the front face of the structure which can make the resistance to contamination excellent in the structure front face demonstrate, ORGANO silicate is hydrolyzed with the water of extent which is not gelled under existence of a hydrolysis catalyst. subsequently, the moisture adjustment constituent which diluted the obtained hydrolysis reactant with the water content diluent, and was adjusted to the predetermined moisture content not only demonstrates the resistance to contamination which demonstrated the hydrophilic property and was excellent from immediately after paint, but A header and this invention were completed for it having storage stability and drying, excelling in handling nature, it excelling also in the adhesion and transparency over a hardening paint film moreover, and the good paint film of an appearance being formed.

[0009] Therefore, while the object of this invention can make the resistance to contamination which could give the hydrophilic property to the structure front face from immediately after paint, and was excellent in the structure front face with this demonstrate, without needing special processing of acid treatment etc. It is in offering the paint agent constituent for pollution controls on the front face of the structure which has drying [excellent in coincidence / storage stability or drying], is excellent in handling nature, is moreover excellent also in adhesion or transparency, and can form the good paint film of an appearance.

[0010] Moreover, other objects of this invention are to offer the manufacture approach of the paint agent constituent for pollution controls on the front face of the structure which can give a hydrophilic property to a structure front face from immediately after paint, without needing special processing of acid treatment etc., is excellent in resistance to contamination, storage stability, handling nature, adhesion, and transparency, and can form the good paint film of an appearance.

[Translation done.]

* NOTICES *

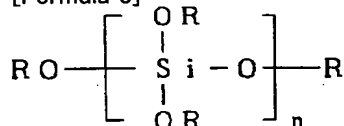
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MEANS

[Means for Solving the Problem] That is, this invention is the following general formula (1).

[Formula 3]



(However, among the formula, R shows the hydrocarbon group of carbon numbers 1-10, and even if it is mutually the same, it may differ.) moreover, n shows one or more integers. The ORGANO silicate expressed is hydrolyzed with the water of the hydrolysis moisture content of the 60 - 600 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of a hydrolysis catalyst. Moisture adjustment is carried out so that a water content diluent may be added to the obtained hydrolysis reactant and the moisture content after adjustment may serve as the range of the 600 - 4000 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate. It is a paint agent constituent for pollution controls on the front face of the structure which contains the obtained moisture adjustment constituent as a principal component. Moreover, this invention is the manufacture approach of the paint agent constituent for pollution controls on such a front face of the structure.

[0012] In this invention, as ORGANO silicate expressed with a general formula (1) An alkyl group, an allyl group, an aryl group, etc. are illustrated as the hydrocarbon group R. More specifically As an alkyl group, for example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, tert-butyl, n-pentyl radical, A vinyl group etc. can be mentioned [as an iso-pentyl radical, a neo-pentyl radical n-hexyl group, an iso-hexyl group, etc. and an allyl group], respectively as a phenyl group, a toluyl radical, a xylyl group, a naphthyl group, etc. and an aryl group. It is the alkyl group of carbon numbers 1-4 especially preferably from a viewpoint of being easy to hydrolyze in these.

[0013] Moreover, about the above-mentioned ORGANO silicate, it may be the monomer of n= 1, it may be the condensation product of n=2-10, or you may be such mixture further.

[0014] The paint agent constituent for pollution controls of this invention hydrolyzes the above-mentioned ORGANO silicate with the water of the hydrolysis moisture content of the 60 - 600 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate under existence of a hydrolysis catalyst. Carry out moisture adjustment and let the obtained moisture adjustment constituent be a principal component so that you may add a water content diluent to the obtained hydrolysis reactant and the moisture content after adjustment may serve as the range of the 600 - 4000 weight section to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate.

[0015] the hydrolysis moisture content used for hydrolyzing this ORGANO silicate here -- " -- it is the amount which is extent which is more than the amount of theory in which 60 - 600 weight section" can hydrolyze this ORGANO silicate thoroughly, and the obtained hydrolysis reactant does not gel to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate, and it is preferably good that they are below the 400 weight sections more than the 120 weight sections. Since it will become easy to gel a hydrolysis reactant if hydrolysis will not fully progress if there are few these hydrolysis moisture contents than 60 weight sections, but the problem that a desired hydrophilic property is not acquired arises and it increases more than the 600 weight sections reversely, it is not desirable. In addition, in case this hydrolysis moisture content hydrolyzes ORGANO silicate, it means the amount of the total moisture which exists in that system of reaction, and it means all the moisture contents not only containing the water added by the hydrolysis system of reaction as a reaction agent but the water introduced into this hydrolysis system of reaction with a hydrolysis catalyst or a reaction solvent.

[0016] Moreover, as a hydrolysis catalyst used for the hydrolysis reaction of ORGANO silicate, although there is especially no limit, they are acid catalysts, such as organic acids, such as mineral acids, such as a nitric acid, a sulfuric acid, a hydrochloric acid, and phosphoric acid, and formic acid, an acetic acid, preferably. In the case of an acid catalyst, if it is usually 0.05 - 2 % of the weight preferably 0.01 to 5% of the weight, the problem that a hydrolysis rate becomes slow will arise in the system of reaction if fewer than 0.01 % of the weight, and the amount of this hydrolysis catalyst used increases more than 5 % of the weight reversely, a hydrolysis reactant will become easy to gel it, and also the problem that control of a reaction becomes difficult produces it.

[0017] Furthermore, if it is good to use the reaction solvent in which the ORGANO silicate and water of the system of reaction are made to dissolve mutually preferably on the occasion of the hydrolysis reaction of ORGANO silicate and it makes these both of each other dissolve as this reaction solvent, there will be especially no limit, but when the handling nature at the time of paint etc. is taken into consideration, alcohols are preferably good and, specifically, ethyl alcohol, iso-propyl alcohol, butyl alcohol, etc. are desirable. To the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate, it is the 200 - 2000 weight section preferably, and the 100 - 3000 weight section and the problem of being easy to gel if fewer than the 100 weight sections usually arise, and if it increases more than the 3000 weight sections reversely, a reaction will become inadequate, and also the problem that a reaction rate becomes slow produces the amount of this reaction solvent used.

[0018] the hydrolysis reactant obtained by this hydrolysis reaction -- a water content diluent -- adding -- the moisture content after that adjustment -- the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate -- receiving -- the 600 - 4000 weight section -- let preferably the 1000 - 3500 weight section and the moisture adjustment constituent which moisture adjustment was carried out and were obtained be the principal components of

the paint agent constituent for pollution controls on the front face of the structure of this invention so that you may become the range of the 1500 - 3000 weight section more preferably. Here, when there are few moisture contents after this adjustment than the 600 weight sections, an alkoxy group remains eventually, there is a problem that a desired hydrophilic property is not acquired, and if it increases more than the 4000 weight sections reversely, the problem that storage stability falls and a product life becomes short will arise.

[0019] If the water content diluent used for this moisture adjustment melts a hydrolysis reactant and each other's water, there will be especially no limit, but when it is good to use the thing of an organic solvent-drainage system and it takes the dryness of the paint film after paint into consideration as this organic solvent, alcohols especially ethyl alcohol, iso-propyl alcohol, butyl alcohol, etc. are desirable like the case of a reaction solvent. Moreover, to the paint agent constituent of this invention, other solvents, such as alcohols, such as ethyl alcohol, iso-propyl alcohol, and butyl alcohol, and a solvent with high viscosity, a high solvent of the boiling point, may be added in order to adjust the rate of drying of the object for viscosity control, or a paint film as occasion demands.

[0020] As a structure front face where the paint agent constituent for pollution controls of this invention is applied For example, non-equipment-and-materials front faces, such as concrete, fiber-reinforced concrete, a slate, and glass, Acrylic resin, a fluoro-resin, polyurethane resin, polyester resin, The film fabricated by resin, such as polycarbonate resin, vinyl chloride resin, and polyethylene resin, Organic material front faces, such as resin mold goods, such as a sheet, and rubber goods, and aluminum, Organic inorganic composite front faces, such as organic inorganic composites, such as fiber consolidation resin, are begun further. metal material front faces, such as iron, stainless steel, a zinc steel plate, and a steel plate, — The painted surface which prepared beforehand the coat chosen from a fluoro-resin coating, polyurethane resin enamels and varnishes, acrylic plastic paint, a polyester resin coating, and aqueous plastic paint in the front face of these inorganic material, organic material, and organic inorganic composite can be mentioned. In these structure front faces, you may paint, after painting the paint agent constituent of this invention directly and carrying out surface treatment, such as a primer, or after carrying out an under coat.

[0021] The paint agent constituent for pollution controls of this invention For example, a structural skin panel, tentorium, A tarpaulin, a windshield sheet, a structural sheet, roofing, a skylight, a concrete wall, Structural members, such as a flush tank, a tank, a shutter, and a sash, a building outer wall, By painting in the part which the dirt of various outdoor articles, such as route members, such as a guard rail, a footbridge, an outer casing, a translucent plate, a noise buffer wall, an indicator, a high-speed path road-side wall, a tunnel wall surface, a railroad viaduct, and a bridge, tends to generate, it can continue extremely at a long period of time, and generating of dirt can be prevented.

[0022] The paint agent constituent for pollution controls of this invention can be easily painted by the paint by the usual method of application, for example, brush coating, roller coating, spray coating, the flow coater, the gravure coating machine, and the spin coat etc. Moreover, although ordinary temperature is sufficient as the desiccation approach and it may be heated, a dry paint film is obtained for the heated direction for a short period of time.

[0023] In the paint agent constituent for pollution controls of this invention, in spite of containing a lot of water Although the reason which exists in stability is not necessarily clear, without a hydrolysis reactant gelling If the polycondensation of the ORGANO silicate is beforehand hydrolyzed and carried out with the reaction water which is extent which hydrolyzes ORGANO silicate thoroughly and a hydrolysis reactant does not gel Although a polymerization reaction progresses and the hydrolysis reactant of this colloidal state forms a polymerization object in the beginning when the hydrolysis product generated by the reaction in the hydrolysis reactant will be in a spherical colloidal state, it distributes in a water content solvent and a lot of water is added here It is thought that this polymerization object exists in stability comparatively although static reaction with the water which exists so much hydrolyzes and a lot of water as a result exists.

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EXAMPLE

[Example] Hereafter, based on an example and the example of a comparison, this invention is explained concretely. In 1500ml three necked flask of examples, taught 40g (the trade name by Tama chemical-industry incorporated company: ES-40, average degree of polymerization 4-5) of oligomer objects of ethyl silicate, and ethanol 88g, mixed to homogeneity, added 21.6g of pure water, and 28g of 6wt%-nitric acids as a catalyst here, and it was made to react to the bottom of heating reflux for 4 hours, it cooled, and the hydrolysis reactant (the 1st reactant) was obtained.

[0025] Next, the water content diluent obtained in the 1st obtained reactant by fully carrying out churning mixing of isopropyl alcohol 190g and the 430g of the pure water was added, churning mixing was carried out further, and it considered as the paint agent constituent of an example 1.

[0026] It replaced with ES-40 in the example 2 1st reaction mixture, and the paint agent constituent of an example 2 was prepared like the example 1 except having added 31.4g (the trade name by Tama chemical-industry incorporated company: MS-51, average degree of polymerization 3-4) of oligomer objects of methyl silicate.

[0027] The paint agent constituent of an example 3 was prepared like the example 1 except having set the pure water in an example 3 water content diluent to 272g.

[0028] The paint agent constituent of an example 4 was prepared like the example 1 except having set the pure water in an example 4 water content diluent to 112g.

[0029] The paint agent constituent of an example 5 was prepared like the example 1 except having set the pure water in an example 5 water content diluent to 48g.

[0030] Although prepared 40g, ethanol 88g, isopropyl alcohol 190g, and 650g of pure water, ES-40 were mixed to homogeneity, 28g of 6wt%-nitric acids was subsequently added in 11500ml three necked flask of examples of a comparison and it was made to react to the bottom of heating reflux for 4 hours, reaction mixture was gelled on the way.

[0031] Unlike the water content diluent used in the example of comparison 2 example 1, the paint agent constituent of the example 2 of a comparison was prepared like the example 1 except having used only isopropyl alcohol 19g as a diluent.

[0032] It verified about each paint agent constituent of the [verification of test-result/example] above-mentioned examples 1-5, and the example 2 of a comparison. after putting storage stability into a container, sealing a paint agent constituent and holding for three months at the temperature of 40 degrees C — a room temperature — returning — the condition in a container — observing — O: — O: in which change is not accepted at all — a little — the white taste — **** and **: — it becomes muddy white and evaluated in four steps of ** of which x:gelation was done. Moreover, the paint agent constituent was painted on the glass plate, and drying, transparency, and an appearance were observed visually. Membranes are not dried and formed 1 hour after x:, but it evaluates in two steps of **. And it dried and formed membranes thoroughly 1 hour after O: about drying, about transparency O The three-stage of ** which wears the white taste 1 hour after x: which becomes transparency 1 hour after : and which wears the white taste a little 1 hour after **: estimated, and it evaluated in two steps of ** powdered without having formed membranes thoroughly 1 hour after O: about the paint film appearance, and drying and forming membranes 1 hour after x:. The above result is shown in a table 1.

[0033]

[A table 1]

| | 調整後水分量(*1) | 貯蔵安定性 | 乾燥性 | 透明性 | 塗膜外観 |
|-------|------------|--------|-----|-----|------|
| 実施例 1 | 3000 | ◎ | ◎ | ◎ | ◎ |
| 〃 2 | 〃 | ◎ | ◎ | ◎ | ◎ |
| 〃 3 | 2000 | ◎ | ◎ | ◎ | ◎ |
| 〃 4 | 1000 | ○ | ◎ | ◎ | ◎ |
| 〃 5 | 600 | △ | ◎ | △ | ◎ |
| 比較例 1 | 4000 | 合成時ゲル化 | | | |
| 〃 2 | 300 | × | × | × | × |

(注) *1) 原料オルガノシリケート中 Si 原子の SiO₂ 換算 100 重量部に対する調整後水分量 (重量部)

[0034] Furthermore, as shown in a table 2, on the substrate with which a solvent fluororesin coating, solvent polyurethane resin enamels and varnishes, the printing fluororesin coating, and the printing polyester resin coating were applied, respectively, the aluminum plate, the vinyl chloride plate, or the polycarbonate plate, the paint agent constituent of each above-mentioned examples 1-6 and the example 2 of a comparison was painted at a rate of 0.03kg/m², and the test piece of examples 1-5 and the example 2 of a comparison was prepared.

[0035] About the test piece of each acquired examples 1-5 and the example 2 of a comparison, the painted surface is exposed to the outdoors, and it is ***** about a direct weathering test. Assessment of the dirt by this direct weathering test made **L* the difference of the lightness exposure [six months after] before and after exposure. The color color difference meter (CR[by Minolta Co., Ltd.]- 300) performed measurement of this lightness difference, and more than O:-2, O:-2-5, **:5-8, and the criteria not more than x:-8 estimated. In addition, lightness difference **L* shows that dirt has few bigger numeric values.

[0036] Moreover, the initial-contact angle in front of an outdoor exposure was measured as a degree of a hydrophilic property. Measurement of this contact angle trickled 0.02 cc deionized water on the above-mentioned painted surface, and measured the contact angle of waterdrop at 20 degrees C using the contact angle measuring device (the trade name by consonance chemistry incorporated company: CONTACT-ANGLEMETER CA-A mold). The result of these three-point measurement averages is shown in a table 2.

[0037]

[A table 2]

| | | 実 施 例 | | | | | 比較例 |
|------------------|------|-------|----|----|----|----|-----|
| | | 1 | 2 | 3 | 4 | 5 | 2 |
| 溶剤フッ素 樹脂塗料 | 接触角 | 28 | 36 | 36 | 58 | 81 | 92 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ○ | △ | × |
| 溶剤ポリウレタン 樹脂塗料 | 接触角 | 37 | 33 | 65 | 65 | 78 | 88 |
| | 屋外暴露 | ◎ | ◎ | ○ | ○ | △ | × |
| 焼付フッ素 樹脂塗料 | 接触角 | 40 | 31 | 48 | 50 | 75 | 93 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ○ | △ | × |
| 焼付ポリウレタン 樹脂塗料 | 接触角 | 15 | 23 | 45 | 52 | 78 | 93 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ○ | △ | × |
| アルミ板 | 接触角 | 35 | 35 | 55 | 53 | 75 | 89 |
| | 屋外暴露 | ◎ | ◎ | ○ | ○ | △ | × |
| 硬質塩ビ板 | 接触角 | 33 | 35 | 53 | 55 | 75 | 95 |
| | 屋外暴露 | ◎ | ◎ | ○ | ○ | △ | × |
| ポリカーボネート 板 | 接触角 | 10 | 10 | 34 | 38 | 70 | 90 |
| | 屋外暴露 | ◎ | ◎ | ◎ | ◎ | △ | △ |

[0038] Since the paint film from which the paint agent constituent of each examples 1-5 was obtained using this is a hydrophilic property so that clearly from the result of the above-mentioned table 1 and a table 2, dirt will be permuted by this storm sewage by hitting, storm sewage will flow and fall, resistance to contamination continues, and is demonstrated at a long period of time, and contamination on the front face of the structure can be prevented effectively.

[0039] The 40g of the same oligomer objects of ethyl silicate as having used in the example 1 into 32000ml three necked flask of examples of a comparison, Teach ethanol 88g and isopropyl alcohol 190g, and it mixes to homogeneity. Add 453g of pure water, and 28g of 6wt%-nitric acids as a catalyst here, and it was made to react to the bottom of heating reflux for 4 hours, and it cooled and the hydrolysis reactant (paint agent constituent) whose moisture content is the 3000 weight sections eventually was obtained to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate.

[0040] It replaced with the oligomer object of example of comparison 4 ethyl silicate, and the paint agent constituent of the example 4 of a comparison whose moisture content is the 3000 weight sections eventually was prepared like the example 3 of a comparison to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate except having used 31.4g of oligomer objects of the same methyl silicate with having used in the example 2.

[0041] The paint agent constituent of the example 5 of a comparison whose moisture content is the 2000 weight sections eventually was prepared like the example 3 of a comparison to the SiO₂ conversion 100 weight section of Si atom in ORGANO silicate except having set the amount of example of comparison 5 pure water used to 293g.

[0042] About each paint agent constituent of the [verification of test-result/example] above-mentioned examples 1-3, and the examples 3-5 of a comparison, the adhesion, the initial hydrophilic property (contact angle), and the appearance of the paint film before and behind a three-month outdoor exposure and a hydrophilic property (contact angle) were evaluated, and the appearance of the paint film before and behind a six-month outdoor exposure, assessment (lightness difference **L*) of dirt, and a hydrophilic property (contact angle) were verified further. A result is shown in a table 3.

[0043] Under the present circumstances, measurement of outdoor-exposure, contact angle, and lightness difference **L* and assessment of a paint film appearance On a substrate, apply a solvent fluororesin coating (the trade name by coating A; Atomix Co., Ltd.: atom SEFURONH), or solvent polyurethane resin enamels and varnishes (the trade name by coating B; Atomix Co., Ltd.: life tex #70) on condition that 30-micrometer coating [1 time], respectively, and a painted surface is formed. The paint agent constituent of each above-mentioned examples 1-3 and the examples 3-5 of a comparison was painted at a rate of 0.03 g/m² on this painted surface, and it carried out by preparing the test piece of each examples 1-3 and the examples 3-5 of a comparison.

[0044] About adhesion, in addition, about the test piece of each above-mentioned examples 1-3 and the examples 3-5 of a comparison According to JIS K5400 8.5.3, it measures by the X cut tape method. 10 : There is no peeling in 8:intersection when peeling is not accepted at all, and peeling is slightly accepted in X cut section. Peeling of 1.5mm or less is accepted in the direction of either from the intersection of the 6:X cut section. 4: The viewpoint with which exceed 1.5mm in the direction of either from the intersection of X cut section, and peeling of 3.0mm or less is accepted to be and peeling is accepted to be to the great portion of 2:X cut section of separating more greatly than the 0:X cut section estimated.

[0045] moreover, the test piece (the include angle between a vertical plane and an inclined plane: 135 degrees) which has a vertical plane in the lower part while a direct weathering test has a 45-degree inclined plane in the upper part, as shown in drawing 1 -- preparing -- a vertical plane -- the appearance of a paint film -- moreover, the dirt of a paint film was evaluated in the inclined plane, respectively. the appearance of the paint film after this outdoor exposure -- visual observation -- O: -- O: in which a rain trace is not accepted at all -- **: a thin rain trace is accepted to be to a part -- it evaluated in four steps of ** where a rain trace is accepted all over [on which the rain trace which clarified to the part is accepted] x:.

[0046]

[A table 3]

| | | | 実施例 | | | 比較例 | | |
|------|---------------------------------------|--------|------|------|------|------|------|------|
| | | | 1 | 2 | 3 | 3 | 4 | 5 |
| 塗料 A | 密着性 | | 10 | 10 | 10 | 8 | 8 | 8 |
| | 接触角 | 初期 | 28 | 36 | 36 | 80 | 81 | 81 |
| | | 3ヶ月暴露後 | 25 | 30 | 32 | 76 | 78 | 79 |
| | | 6ヶ月暴露後 | 17 | 25 | 25 | 65 | 65 | 67 |
| | 塗膜の外観 (*1) | 3ヶ月暴露後 | ◎ | ◎ | ◎ | × | × | × |
| | | 6ヶ月暴露後 | ◎ | ◎ | ◎ | △ | △ | △ |
| | 6ヶ月暴露前後の汚れ評価 (明度差 ΔL^*) (*2) | | -0.4 | -0.8 | -0.9 | -5.7 | -5.8 | -6.7 |
| 塗料 B | 密着性 | | 10 | 10 | 10 | 0 | 4 | 6 |
| | 接触角 | 初期 | 37 | 33 | 65 | 79 | 79 | 81 |
| | | 3ヶ月暴露後 | 25 | 29 | 45 | 77 | 77 | 78 |
| | | 6ヶ月暴露後 | 18 | 24 | 35 | 65 | 66 | 68 |
| | 塗膜の外観 (*1) | 3ヶ月暴露後 | ◎ | ◎ | ○ | × | × | × |
| | | 6ヶ月暴露後 | ◎ | ◎ | ◎ | △ | △ | △ |
| | 6ヶ月暴露前後の汚れ評価 (明度差 ΔL^*) (*2) | | -0.3 | -0.3 | -1.2 | -6.0 | -6.0 | -6.5 |

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the explanatory view showing the configuration of the test piece used when evaluating the appearance of a paint film, and the dirt of a paint film in a direct weathering test.

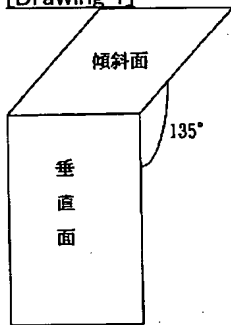
[Translation done.]

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DRAWINGS

[Drawing 1]

[Translation done.]